



Characterization and prediction of monomer-based dose rate effects in electron-beam polymerization



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ABSTRACT

Properties of some materials produced by electron-beam (EB) induced polymerization appear dependent upon the rate at which the initiating dose was delivered. However, the magnitude of these dose rate effects (DREs) can vary greatly with different monomer formulations, suggesting DREs are dependent on chemical structure. The relationship among dose, dose rate, conversion, and the glass transition temperature (T_g) of the cured material was explored for an acrylate monomer series. A strong correlation was determined between the DRE magnitude and monomer size, and this correlation may be attributed to chain transfer. Using the T_g shift caused by changes in dose, a preliminary predictive relationship was developed to estimate the magnitude of the T_g DRE, enabling scale-up of process variables for polymers prone to dose rate effects.

1. Introduction

Electron-beam (EB) polymerization is used extensively to produce millions of tons of film, coating, ink, and adhesive products each year (Cohen, 2012). EB curing is a rapid, sustainable process, requiring no environmentally damaging solvents and less energy than thermal polymerization methods (Datta et al., 1998; Drobny, 2013; Kinstle, 1990). Furthermore, in contrast to photopolymerization, EB polymerization is not hindered by fillers or pigments, allowing for widespread property tuning through the use of additives (Seto et al., 1985).

In spite of the established commercial use of EB-curing technology, published research describing the fundamental aspects of EB polymerization is limited, especially in comparison to photopolymerization and thermal polymerization (Davidson et al., 1987; Patacz et al., 2000). Large gaps exist in understanding how EB-cured polymer properties are influenced by monomer chemistry and processing variables, preventing the establishment of a structure/processing conditions/properties relationship. One area where this knowledge gap is especially problematic is the application of dose rate and how dose rate affects polymer properties.

EB radiation is of sufficient energy to create radicals from monomer molecules without the presence of initiators. A given dose (i.e., the amount of energy deposited in materials) is needed to achieve adequate

conversion of the monomers and oligomers into polymer. While the dose can be held constant by adjusting the beam current and line speed (see Eq. (1)), the speed at which the dose is delivered – dose rate –

$$Dose = \frac{Beam\ Current * K}{Line\ Speed} \quad (1)$$

Altering the dose rate can cause property changes in the cured polymer, known as dose rate effects. For example, studies have correlated dose rate to the polymerization rate and molecular weight of polymers formed via radiation-initiated radical polymerization (Chapiro, 1962; Siyam, 1997; Woods and Pikaev, 1994). Dose rate effects are not unique to EB polymerization nor are they a new concept. The effects of dose rate have also been extensively studied in visible/UV photopolymerization (where dose rate is more appropriately termed exposure rate) as exposure reciprocity law failures (Emami and Söderholm, 2003; Hadis et al., 2011; Martin et al., 2003; Wydra et al., 2014). Other applications where dose rate effects have been studied include gamma-irradiated polymer systems, such as those undergoing decomposition (Seguchi et al., 1977), grafting (Abdel-Bary and El-Nesr, 1997), or polymerization (Hashimoto et al., 1976). In EB polymerization systems, where monomer is converted to polymer, some studies have reported dose rate effects (Batsberg-Pedersen and Singer, 1972; Rangwalla and

Abbreviations: BA, benzyl acrylate; DE, dose effect; DMA, dynamic mechanical analysis; DMPA, 2,2-dimethoxy-2-phenylacetophenone; DRE, dose rate effects; EB, electron beam; HPOPA, 2-hydroxy-3-phenoxypropyl acrylate; PA, phenyl acrylate; PEA, 2-phenylethyl acrylate; PET, polyethylene terephthalate; POEA, 2-phenoxyethyl acrylate; R_p , rate of polymerization; R_t , rate of termination; R_{ct} , rate of chain transfer; T_g , glass transition temperature

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Nablo, 1990; Xiancong et al., 2008). However, dose rate effects in these EB polymerization systems have not been systematically studied over a wide range of processing conditions and monomer structures.

Dose rate effects point to changes in the polymer network, and controlling these effects could be beneficial in advancing EB polymerization. Currently, EB polymerization is restricted to applications needing or allowing a highly cross-linked network, which is formed as a result of the many side reactions caused by electron-induced free-radical formation. If manipulating dose rate causes changes in the polymer network, it could be the additional variable needed to control network formation. However, some formulations are more prone to dose rate effects than others, suggesting formulation chemistry has an impact on the magnitude of the dose rate effects.

Furthermore, avoiding dose rate effects, particularly in commercial applications, may be difficult. Many new formulations are tested on a slower pilot line or lab equipment, where the materials and required dose levels are optimized. Then, the beam current and line speed are scaled for commercial production requirements. If dose rate effects and their magnitude were consistent, adjustments could be made during this scale-up process; however, as of yet, no fundamental understanding of how dose rate effects are governed by processing variables and formulation chemistry has been established.

In this study, a series of acrylate monomers was investigated, and a strong correlation was discovered between monomer chemical structure and the magnitude of the dose rate effect found in two, commonly reported polymer properties: conversion and glass transition temperature. From these data, a rudimentary structure/processing conditions/properties relationship was established, enabling predictions of a formulation's dose rate effect by comparing its response to different doses. This foundational research will allow more thorough investigations into the cause of dose rate effects in EB-cured polymers, providing a more reliable means of scaling to production modes.

2. Experimental

2.1. Materials

A series of five monomers was chosen to investigate the impact of monomer chemistry on the magnitude of the dose rate effect: phenyl acrylate (PA, MP Biomedicals), benzyl acrylate (BA, MP Biomedicals), 2-phenylethyl acrylate (PEA, Polysciences), 2-phenoxyethyl acrylate (POEA, TCI America), and 2-hydroxy-3-phenoxypropyl acrylate (HPOPA, Sartomer) (Fig. 1).

To enable Raman conversion measurements, each monomer contains a phenyl group and an acrylate moiety (Schissel et al., 2014). The number of chemical bonds separating the phenyl ring from the acrylate moiety differentiates the monomers and is incrementally increased across the series. An aliphatic urethane diacrylate oligomer, Ebecryl 8807 (proprietary structure, Allnex), was added to each monomer to improve the film properties of the samples and allowed for mechanical-property testing. All materials were used as received and stored at room temperature.

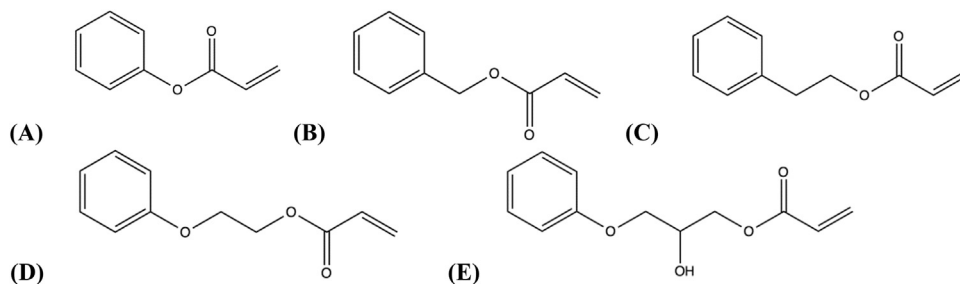


Fig. 1. The chemical structures of the 5-monomer series: (A) PA, (B) BA, (C) PEA, (D) POEA, and (E) HPOPA.

2.2. Methods

2.2.1. EB film preparation

Each formulation consisted of a 50/50, by weight, mixture of monomer and oligomer. Because of the high viscosity of the oligomer, the formulations were heated to approximately 60 °C to allow mixing of the monomer and oligomer. Once heated, formulations were stirred using a drill with a paddle mixer attachment.

Samples for EB curing were prepared by first treating 4 × 3.25 in. glass slides using two coats of Rain-X® 2-in-1 glass cleaner and rain repellent. Next, two layers of lab tape (total thickness ~ 180 μm) were placed on either side of the glass to be used as spacers. A large droplet, approximately 1 mL, of a formulation was then placed near the top of the slide, between the pieces of tape, and covered with a piece of silicone-coated, 34-μm thick polyethylene terephthalate (PET). A straight edge was drawn across the PET to form a uniform film underneath.

The samples on the glass slides were polymerized by EB irradiation through the PET film using an EB accelerator equipped with a variable-speed, fiberglass carrier web (BroadBeam EP Series, PCT Engineered Systems, Inc.). Three different doses (15, 30, and 60 kGy) and three different line speeds (actual settings of 20, 100, and 200 ft/min, but reported in SI units as 6, 30, and 60 m/min here) were used to cure the films. Beam uniformity was verified using GEX B3 dosimeters (batches BD and CA). Dosimeters were placed in 2.54 cm increments across a 12.7 cm width. Percent variation was 2.2% or less. Accelerating voltage and N₂ flow rate were held constant at 250 kV and 0.48 standard m³/min, respectively. The dose rate for these experiments are presented in Table 1 as calculated using Eq. (2) (Rangwalla and Nablo, 1990):

$$\text{Dose Rate} = \frac{\text{Dose} \cdot \text{Line Speed}}{\text{Length of Irradiation Zone}} \quad (2)$$

where the length of the irradiation zone is 20.3 cm for this instrument.

Once polymerized, the films were removed from the glass slides and cut into rectangles measuring 6.25 × 25 mm for characterization. The use of silanized (Rain-X®-treated) glass and silicone-coated PET assisted in the release of the polymer film. The PET cover was used to eliminate the effect of oxygen diffusion in the experiments.

2.2.2. Raman spectroscopy

2.2.2.1. Polymer conversion. Raman microscopy was used to determine conversion of the polymer films. In order to eliminate error from instrumental variations, a reference peak was used. Previous work has established the reaction peak at 1636 cm⁻¹ (indicative of the -C=C- bond in the acrylate moiety) and the reference peak at 1613 cm⁻¹ (indicative of the -C=C- bonds in the phenyl ring) (Schissel et al., 2014). Conversion, α, was calculated using the following equation:

$$\alpha = \left(1 - \frac{I_{\text{rxn}}(P)/I_{\text{ref}}(P)}{I_{\text{rxn}}(M)/I_{\text{ref}}(M)} \right) * 100 \quad (3)$$

where $I_{\text{rxn}}(P)$ and $I_{\text{ref}}(P)$ are the peak intensities of the reaction and reference peak of the polymer, respectively; $I_{\text{rxn}}(M)$ and $I_{\text{ref}}(M)$ are the peak intensities of the reaction and reference peak of the monomer (Cai and Jessop, 2006).

Raman spectra of the polymerized films were collected using an

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